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Letter Report

Fabrication of Intermetallic Compounds by
Solid State Reaction of Roll-Bonded Materials

Contract No. N00014-85-C-0857

Prepared for:

Office of Naval Research
Arlington, VA 22219

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Quarterly Progress Report (#15)
(MCR-85-721)

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1.0 **Contract Number:**
N00014-85-C-0857

2.0 **Reporting Period:**
2/10/90-5/9/90

3.0 **ONR Scientific Officer:**
Dr. Steven G. Fishman

4.0 **Work Performed At:**
Martin Marietta Astronautics Group, Denver, CO 80201

5.0 **Principal Investigator:**
Dr. William C. Moshier

6.0 **Project Title:**
Fabrication of Intermetallic Compounds by Solid State Reaction of Roll-Bonded Materials

7.0 **Description of Research:**

7.1 **Objectives of Present Research**

- Intermetallic compounds offer very high specific material properties and property retention at elevated temperatures. However, reliable processing techniques to fabricate these materials have not been developed. This program will investigate the use of a novel, low cost fabrication technique involving a deformation-solid state reaction bonding process to form titanium beryllides. The objectives of this investigation are to:

- Establish reaction kinetics for the formation of Ti beryllide intermetallic compounds
- Establish processing parameters needed to reproducibly fabricate these materials
- Characterize the properties of Ti beryllides fabricated using a deformation-solid state reaction bonding process
- Investigate the effects of alloying additions on the crystal structure of Ti beryllides and determine how these changes impact mechanical properties

7.2 **Summary of Work Accomplished During Previous Reporting Period**

- Fabrication of Metal Clad Filaments (MCFs)/Reaction Study

The interaction between Ti and Be was characterized with co-extruded material that was placed into Ta-lined steel cans and reacted under pressure. The Ti/Be molar ratio for this study was 1:2. The starting material was Be fibers that were wrapped with Ti foil. The first extrusion reduced the size of the Be wires from 2.5 mm to 1.1 mm. Testing was conducted on this material to obtain data on the reaction rate, sequence, and rate between Ti and Be. The rate of the reaction was analyzed at only one temperature and one pressure, i.e., 1000°C and 20,000 psi. *JLS* ←

Three individual regions were identified following the heat treatment. The growth of each region in the reaction zone was measured over time, and modeled using a simple power law equation: $x^n = kt$, where x is the zone thickness, n is the order of the reaction, k is the reaction constant, and t is time. Table 1 lists the reaction constants for each region in the reaction zone. Analysis of the reaction zone using Auger electron spectroscopy (AES) and X-ray diffraction (XRD), shown in Figure 1, revealed that three phases were present: $TiBe_2$, $TiBe_3$, and Ti_2Be_{17} .

Table 1. Reaction parameters for the Ti-Be system (see Figure 1b for region references)

Parameter	Region 1	Region 2	Region 3
$k \text{ (cm}^n/\text{s)}$	3.4×10^{-11}	1.2×10^{-10}	1.1×10^{-11}
n	2.7	1.4	1.9

The kinetic data indicated that complete conversion of the material to Ti_2Be_{17} would be possible in less than forty hours, if the Be filament diameter was less than 100 μm . (Note: a complete reaction would have only been possible if the material had a Ti:Be molar ratio of 2:17. In this study, the extruded material was Ti rich, with a Ti:Be ratio of 1:2.) The next step in the study was to reduce the Be filament diameter and completely convert the Be to a beryllide to determine whether it was possible to convert the extrusion to a lower order beryllide in a reasonable period of time. This reduction in filament size was completed after the third extrusion, and the material was reacted.

The Be fibers in the third extrusion were fully converted after two hours at 1000°C and 20,000 psi. Continued heating of the sample resulted in the higher order beryllide, Ti_2Be_{17} , reacting to form the lower order beryllides, $TiBe_2$ and $TiBe_3$. As the Ti_2Be_{17} was consumed, the two lower order beryllides continued to grow. Figure 2 indicates that the higher order beryllide grows rapidly, and the rate of growth diminishes after the Be is consumed. There may be several factors that impact the growth, including the lower diffusion rate of Ti, particularly through the beryllides, and the additional energy required to breakdown the higher order beryllide to form the lower order beryllides.

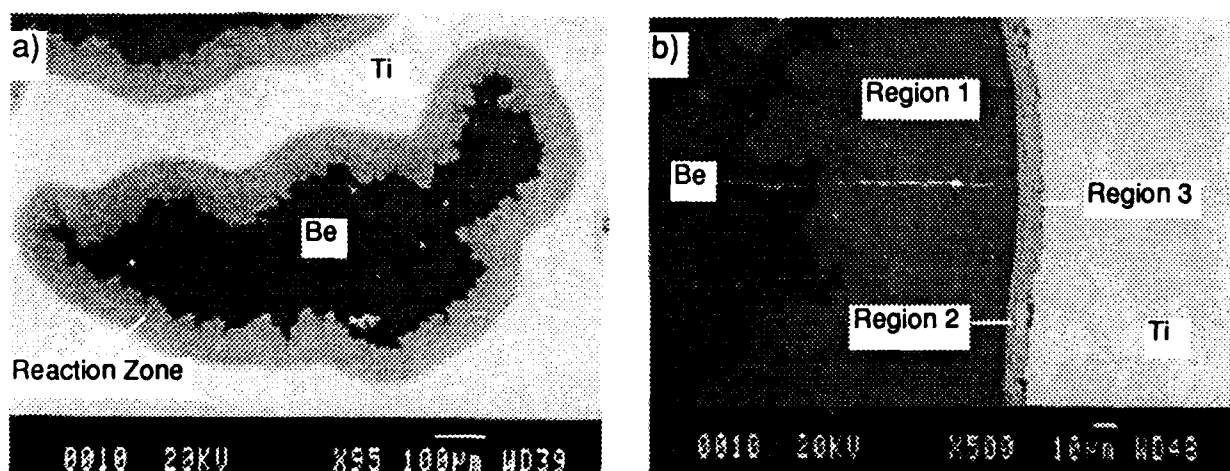


Figure 1. Reaction of Ti matrix and Be fiber from the first extrusion at 1000°C for 24 hours and 20,000 psi. a) Cross-section of the partially reacted Be fiber in a Ti matrix reveals a reaction zone that is free from voids, cracks, or other defects. b) Enlargement of the reaction zone show the presence of three individual regions, labeled region 1, 2, and 3.

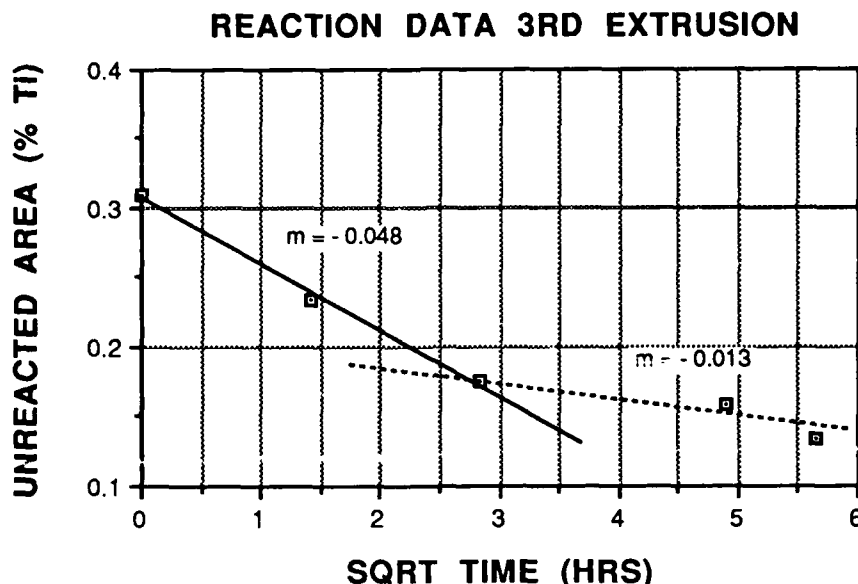


Figure 2. Area of remaining non-reacted Ti matrix as a function of the square root of time in hours, reacted at 1,000°C and 20,000 psi. The data shows that the Ti is quickly consumed at the start of the solid state reaction as Be fiber is converted into the higher order beryllide. After all the Be fiber is reacted, the rate at which the Ti matrix is consumed decreases, as the higher order beryllide must now be converted into lower order beryllides. In this extrusion, with the initial average Be fiber diameter of 100 μm , it would take almost 300 hours at 1000°C to convert the extrusion to TiBe_2 . On the other hand, it would require approximately forty five hours to convert a similar diameter extrusion with the proper mix of Ti and Be to a higher order beryllide.

Upon the completion of this initial study on the MCFs, we have arrived at the following conclusions:

- 1) The solid state reaction between Ti and Be results in the formation of at least three intermetallic compounds: TiBe_2 , TiBe_3 , and $\text{Ti}_2\text{Be}_{17}$.
- 2) The growth of $\text{Ti}_2\text{Be}_{17}$ is rapid, whereas the growth of TiBe_2 and TiBe_3 is slower. The net result of this behavior is the reaction zone, when excess Be is available, consists primarily of $\text{Ti}_2\text{Be}_{17}$. The rate limiting step in the reaction appears to be the interface controlled formation of TiBe_3 .
- 3) After the conversion of all of the Be to a beryllide, the reaction slows as TiBe_2 and TiBe_3 are formed and $\text{Ti}_2\text{Be}_{17}$ is consumed.
- 4) The formation of Ti beryllides using a solid state reaction appears to be better suited for forming $\text{Ti}_2\text{Be}_{17}$, rather than either TiBe_2 or TiBe_3 .

7.3 Progress During the Reporting Period

• Fabrication of Thin Films

The fabrication of beryllide foils by sputtering has been the major focus during this period. The initial effort involved sputtering Be onto Ti, and characterizing the material to determine cleanliness, as well as to develop sensitivity factors capable of differentiating between TiBe_{12} and $\text{Ti}_2\text{Be}_{17}$. Nine Ti sheets 0.33-mm-thick were coated with 25- μm -thick Be film. These samples will be used for roll bonding, which will be described later in this report.

Following the sputter-deposition of the pure Be films onto Ti, the effort shifted to co-sputter depositing Ti and Be onto a Mo-coated Cu substrate to make free-standing beryllide foils. A schematic of the Rf magnetron process used to make foils is shown in Figure 3. The target was fabricated from high purity Be (less than 10 ppm oxygen), and Ti plugs were inserted into the target so that a predicted Ti-Be mixture could be sputter-deposited. The first films were sputtered at room temperature, and their chemistry was determined to be 32.41 w/o Ti and 67.59 w/o Be. This compares to 32.57 w/o and 67.43 w/o for the TiBe_{12} compound mixture.

The structure of the film changed as the substrate temperature increased. Initial efforts to deposit the beryllide onto a substrate at either 20°C or 200°C resulted in amorphous foils. At 500°C, the structure of the film changed, and both TiBe_{12} and $\text{Ti}_2\text{Be}_{17}$ were detected by XRD. Initially, AES detected low levels of oxygen in the film (0.3 a/o), and the films appeared cloudy. Several parameters were changed, such as increasing the sputtering rate, using a Ti substrate to heat the samples, and increasing the pumping rate through the chamber. After changing these processing conditions, no oxygen was detectable in the films with AES, and the films appeared bright and had good luster.

A mask, shown in Figure 4, was used to make several different types of samples, including tensile samples, oxidation resistance samples, and samples for metallographic examination. One of the tensile samples, which is a beryllide film 50- μm -thick, is shown in Figure 5. The sample is 7.5 long and 2.2 cm wide.

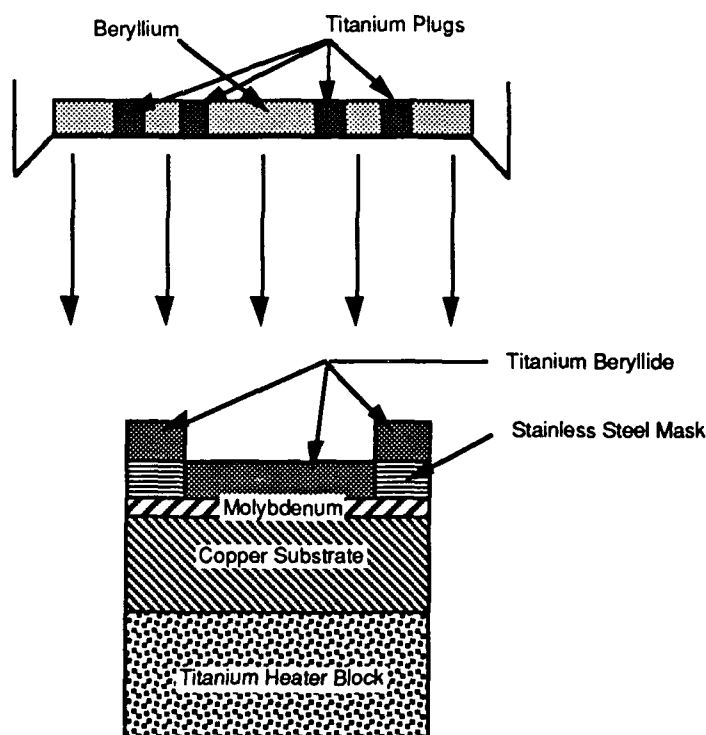


Figure 3. Configuration used to fabricate Ti-Be foils up to 50 μm thick. A Be target with Ti plugs is used to co-sputter the beryllide intermetallic. The beryllide is deposited onto a heated Mo-coated Cu foil. After the sample has cooled sufficiently, it is removed from the sputtering chamber and the Cu foil is etched from the sample. The Mo is used to stop the etchant from reaching the beryllide. The Mo is removed by an alternate etching process so that the free standing film will not be damaged.

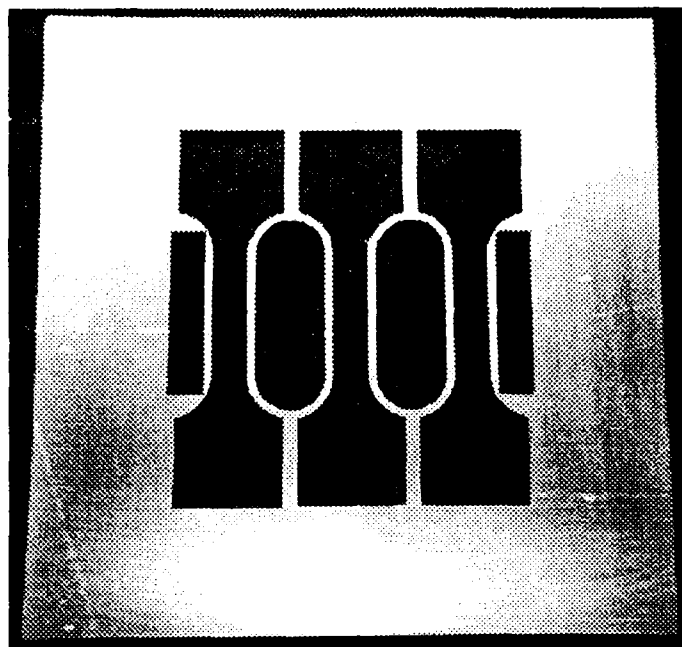


Figure 4. Stainless steel mask used to directly fabricate the test specimens after sputtering, eliminating the need to machine, and potentially damage, the foils after their deposition. The tensile samples are 7.5 cm long and 2.2 cm wide.

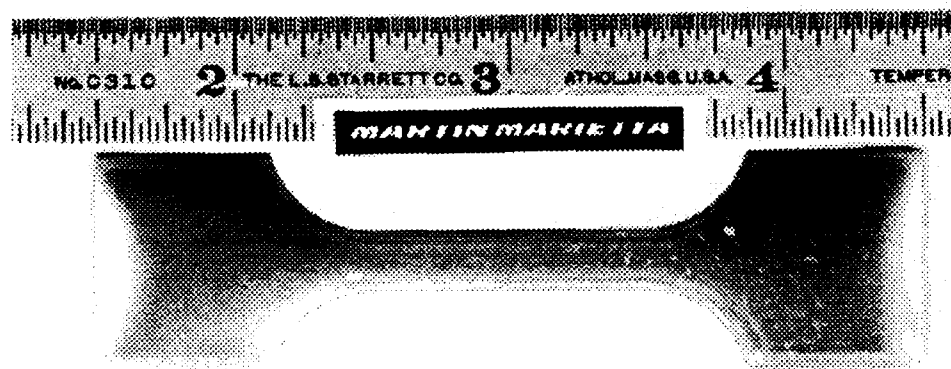


Figure 5. Actual beryllide tensile sample made by co-sputtering Ti and Be together onto a Mo-coated Cu substrate at 500°C, and etching the substrate away from the beryllide to form a free standing film.

7.4 Tasks for the Next Period

- Characterization of Reaction Products in the Second and Third Extrusions.

The effort to fully characterize the reaction products in each extrusion made by NMI will continue. This effort was delayed until a pure source of Be could be made by sputtering so that an accurate sensitivity factor for Be could be obtained. A reliable number for the sensitivity of Be is essential to accurately determine the composition of each reaction zone. The value presently being use is not sufficiently accurate to determine the difference between $TiBe_{12}$ and Ti_2Be_{17} . This work is presently underway and is expected to be completed no later than the middle of May.

- Fabrication of Thin Films

Rocky Flats will complete their sputtering effort. The composition and structure of each test run will be evaluated during the next quarter. Testing will be conducted on both as-deposited and heat treated (homogenized) material. Mechanical testing will be performed initially at room temperature, and subsequent testing will be conducted at 2000°C. Oxidation tests at temperatures up to 1500°C over an 100 hour period will be performed to determine the oxidation behavior of the material. Microstructural evaluation of the films with TEM will be initiated to quantify the important microstructural features of the films.

- Roll Bonded Microlaminated Ti-beryllide Sheets and Monolithic Ti-Be.

Manufacturing Sciences Corporation (MSC) is presently in the process of making both monolithic beryllide sheet and Ti-beryllide laminated sheet. In the case of the laminated Ti-beryllide composite, Be sputter-coated Ti was stacked as shown in Figure 6(a), canned in Ta-lined steel cans, and cross rolled at 750°C to a 25:1 reduction. The can will be etched off of the sample, which is expected to be 0.13-mm-thick.

Monolithic beryllide sheet will be fabricated by stacking layers of Ti and Be sheet into a Ta-lined steel can and cross-rolling the material at 750°C to a 25:1 reduction, see Figure 6(b). The starting material will be commercially pure Ti sheet 0.33-mm-thick and 1.65-mm-thick vacuum arc remelted Be sheet. This system will produce a compound after the solid state reaction that will be a mixture of $TiBe_{12}$ and Ti_2Be_{17} . The final thickness of this beryllide foil made using this process will be 0.33-mm-thick.

Testing of the roll bonded material is not expected to start until after the next quarter.

7.5 Presentations During This Period

- None

7.6 Technical Reports During This Period

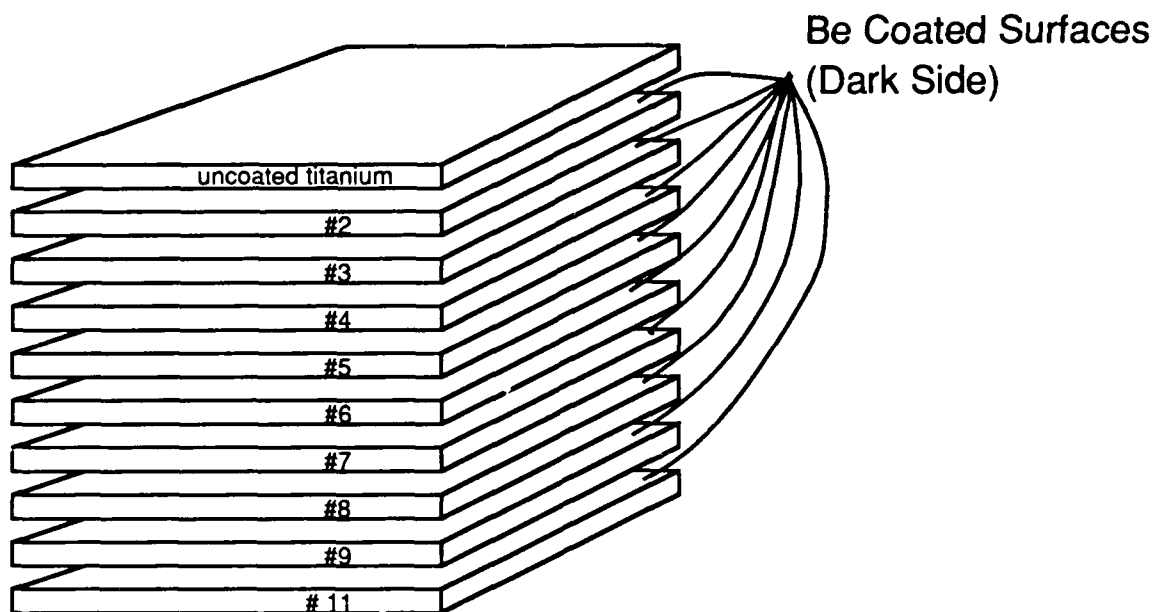
- None

7.7 Publications During This Period

- None

7.8 Participants On The Program (Last Quarter)

a)



b)

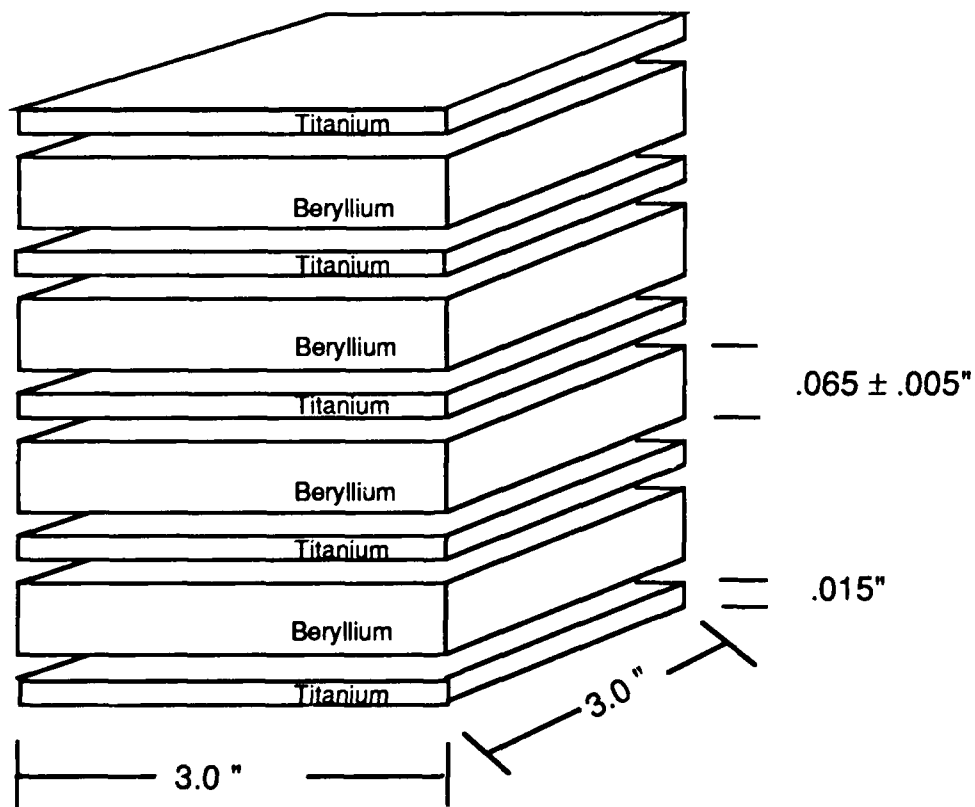


Figure 6. Experimental lay-up of material that will be used to fabricate a) roll bonded Ti-beryllide laminated sheet and b) roll bonded monolithic Ti beryllides.

7.5 Participants on the Program (2/10/90 thru 5/9/90)

Name	Task
Nuclear Metals Inc., Concord, MA.....	Fabricate MCF, Extrusion, Specimen Prep
EG&G, Rocky Flats, Golden, CO.....	Sputter-deposit Be/Ti-Be Films
Manufacturing Sciences Corporation, Oak Ridge, TN.....	Roll Bonding Effort